Advanced Cleans: A Structured Approach

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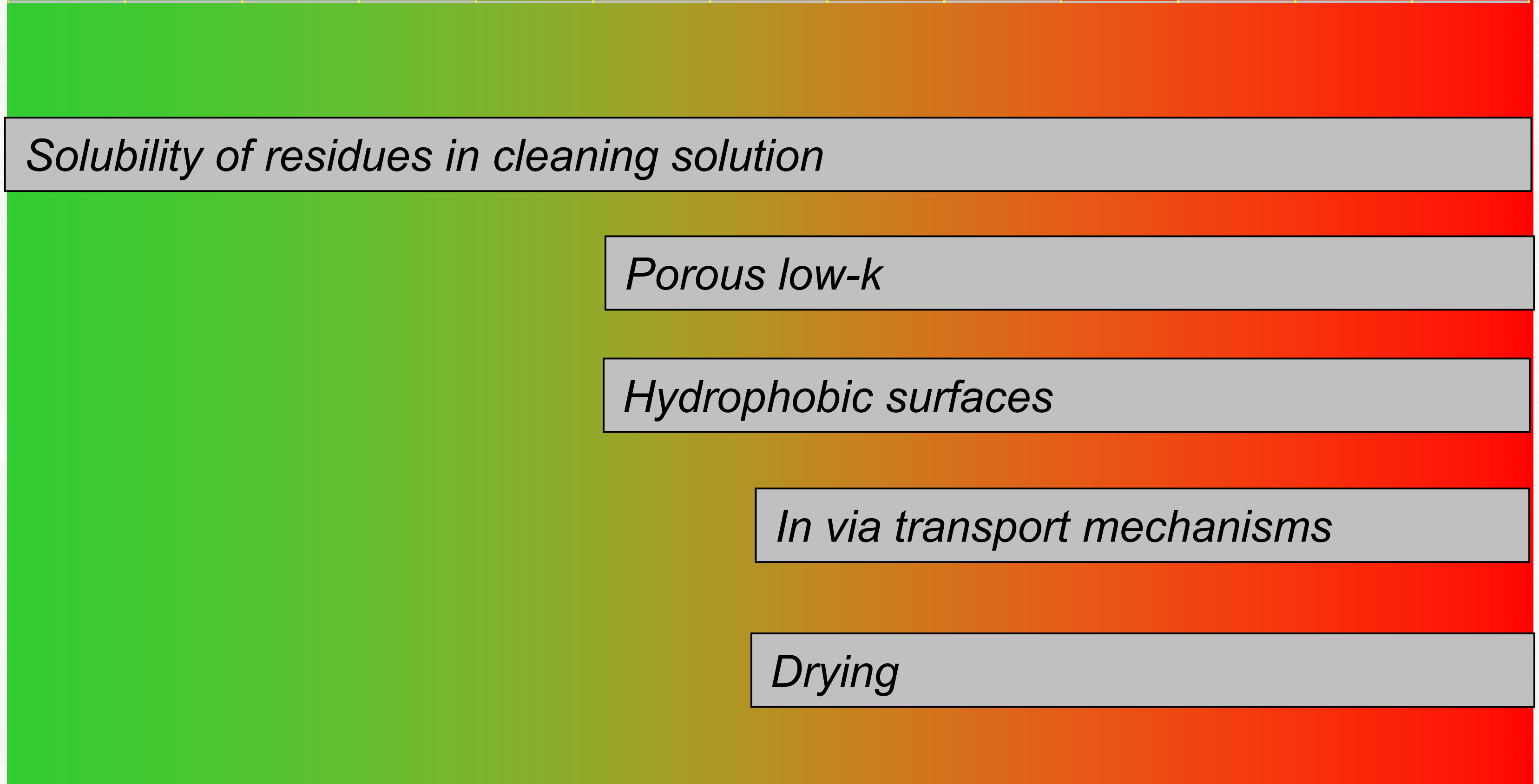
Accelerating the next technology revolution.

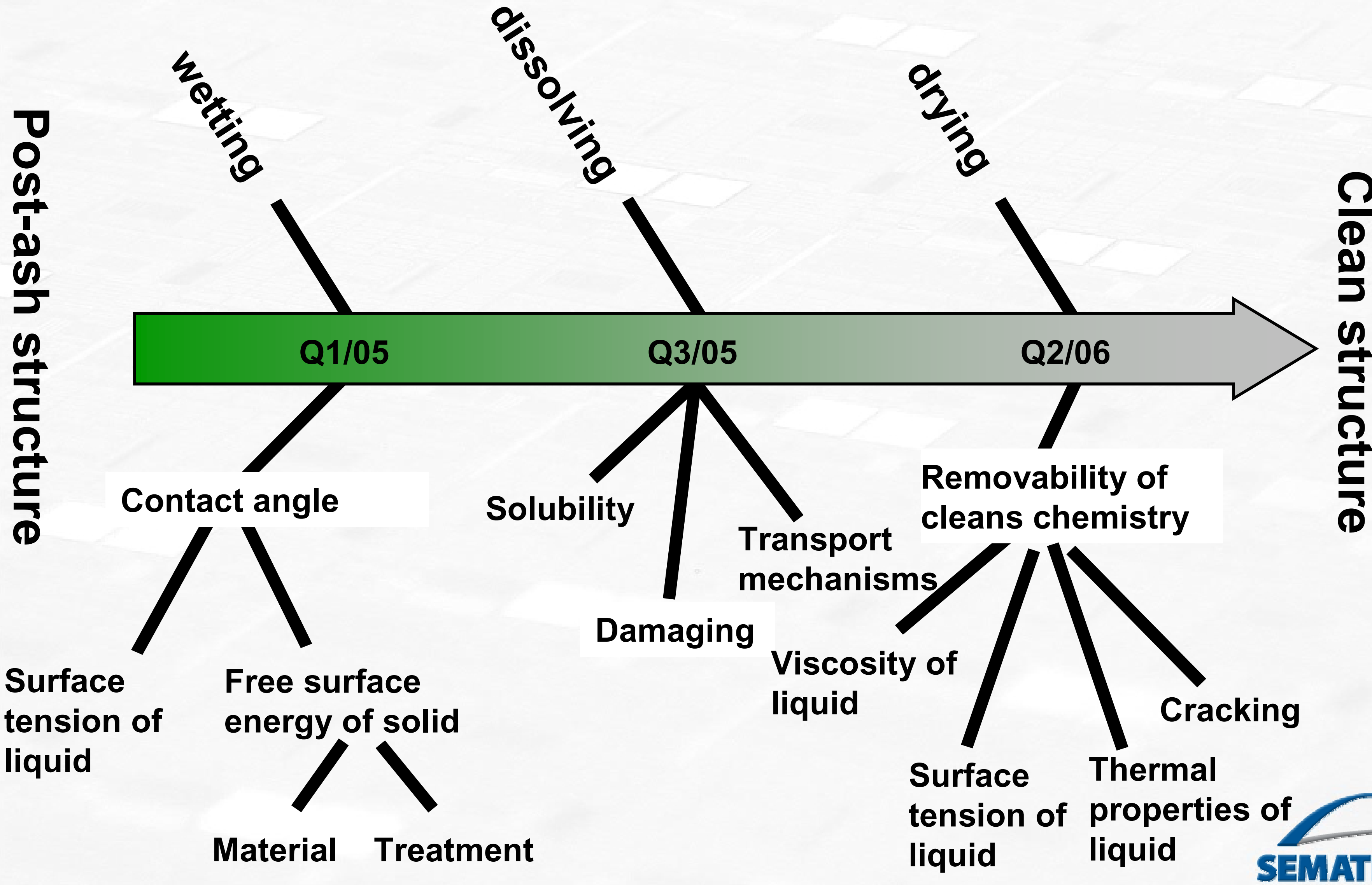
ITRS – cleans challenges

Year of Production	2003	2004	2005	2006	2007	2008	2009	2010	2012	2013	2015	2016	2018
Technology node		hp90			hp65			hp45		hp32		hp22	
approx via size (nm)*	120	107	95	85	76	67	60	54	42	38	30	27	21



*MPU/ASIC ½ Pitch (nm)

The cleans process fragmented: the simple model

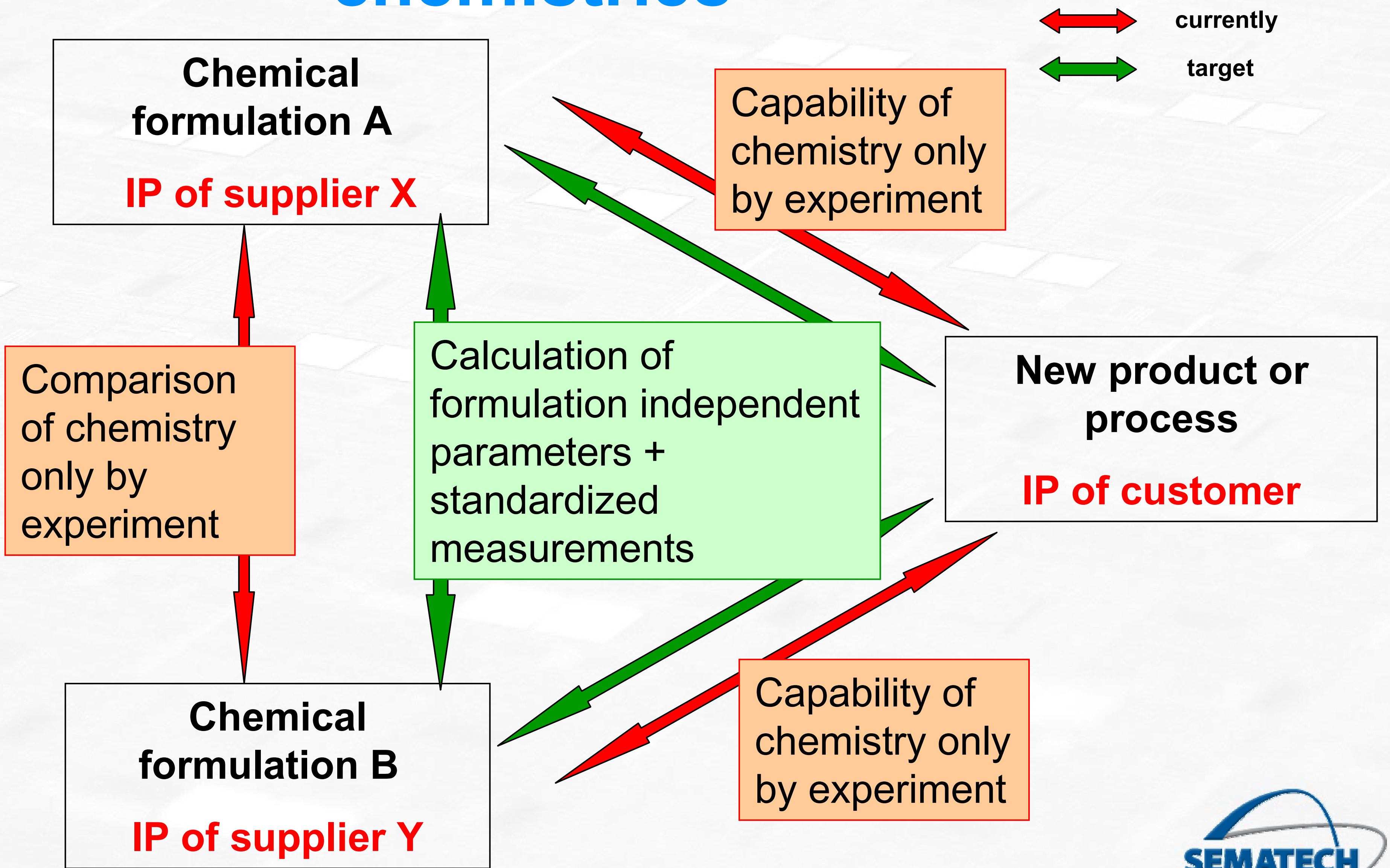


The cleans process fragmented: the full model

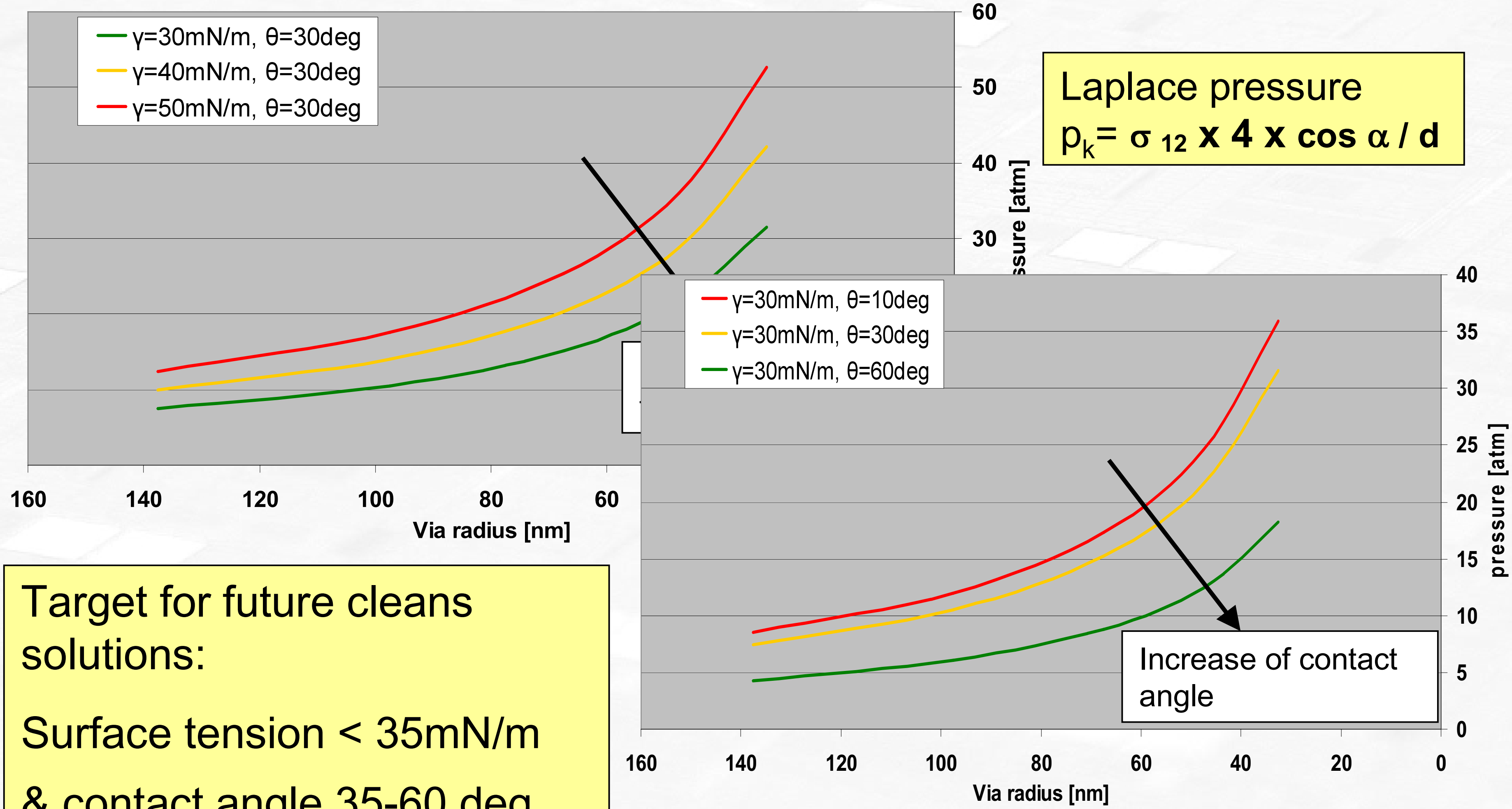
Post-ash structure → Clean structure

		wetting		dissolving						rinsing		drying
	description	cleaning liquid entering structure	cleaning liquid establishing contact to target	mass transport of active compound to the target	adsorption of the active compound to the target	reaction and/or dissolution	desorption of the reaction product	mass transport of reaction product out of structure	mass transport of reaction product away from the structure	mass transport of all cleaning components out of the structure and replace with fluid	(Substitution of the DI by IPA etc. if necessary)	complete remove of DI / IPA, which might contain traces of reaction products
		1.1	1.2	2.1	2.2	2.3	2.4	2.5	2.6	3.1	(3.2)	4.1
depending on	chemistry	-surface tension -viscosity	-surface tension	-mass transport by diffusion -viscosity	-adsorption	-reaction / dissolution -equilibrium state -reaction rates	-desorption	-mass transport by diffusion -viscosity	-viscosity	-mass transport by diffusion -viscosity	-mass transport by diffusion -viscosity	-thermal properties of last rinse fluid -viscosity
depending on	tool	-mechanical agitation -energy input (eg.megasonic)	-energy input (eg.megasonic)	-mass transport by turbulent flow		-energy input (eg.megasonic, photons)		-mass transport by turbulent flow	-mass transport by turbulent / laminar flow	-mass transport by turbulent / laminar flow	-mass transport by turbulent / laminar flow	-energy input photons,heat -mass transport by: -liquid flow -purge gas
depending on	wafer	-feature dimensions -free surface energy	-free surface energy of target	-feature dimensions				-feature dimensions	-feature dimensions -surface structure	-feature dimensions -surface structure	-feature dimensions -surface structure	-feature dimensions -surface structure -free surface energy

Problem: comparison of different chemistries



Future trends for surface tension & contact angles



Laplace pressure

$p_k = \sigma_{12} \times 4 \times \cos\alpha / d$

Target for future cleans solutions:

Surface tension < 35mN/m

& contact angle 35-60 deg

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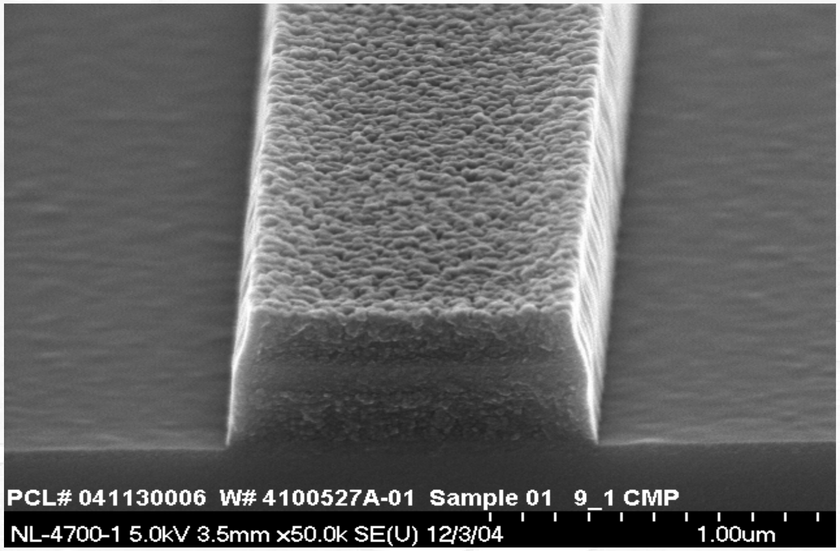
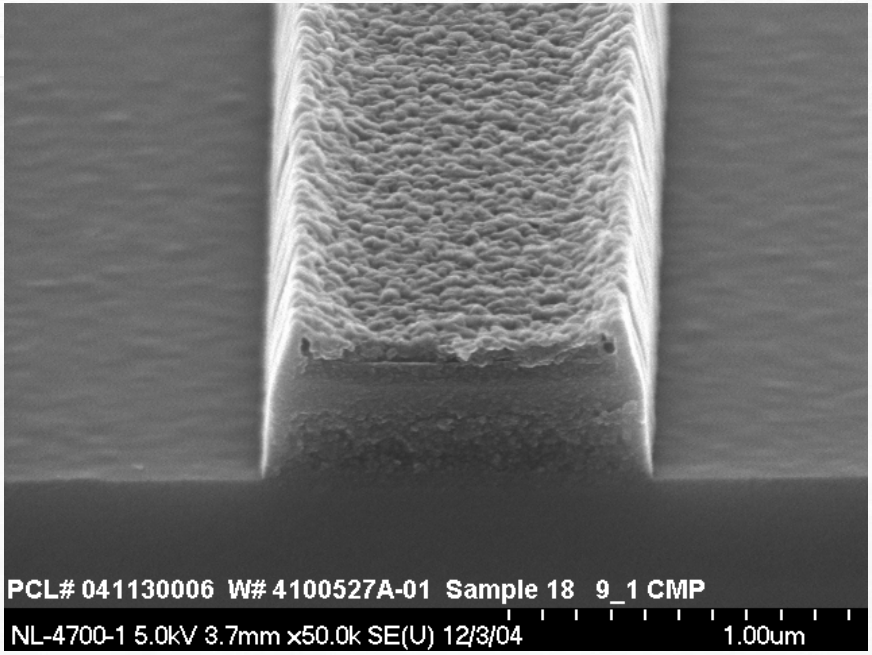
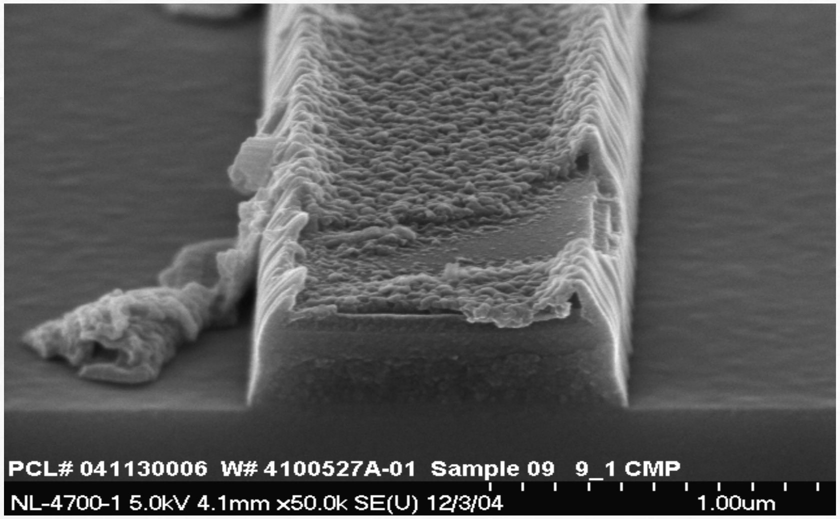
Solubility: resist removal on p-MSQ



DI water: no effect



o-Xylene: minor effect



Chlorobutane: removal of uncrusted resist

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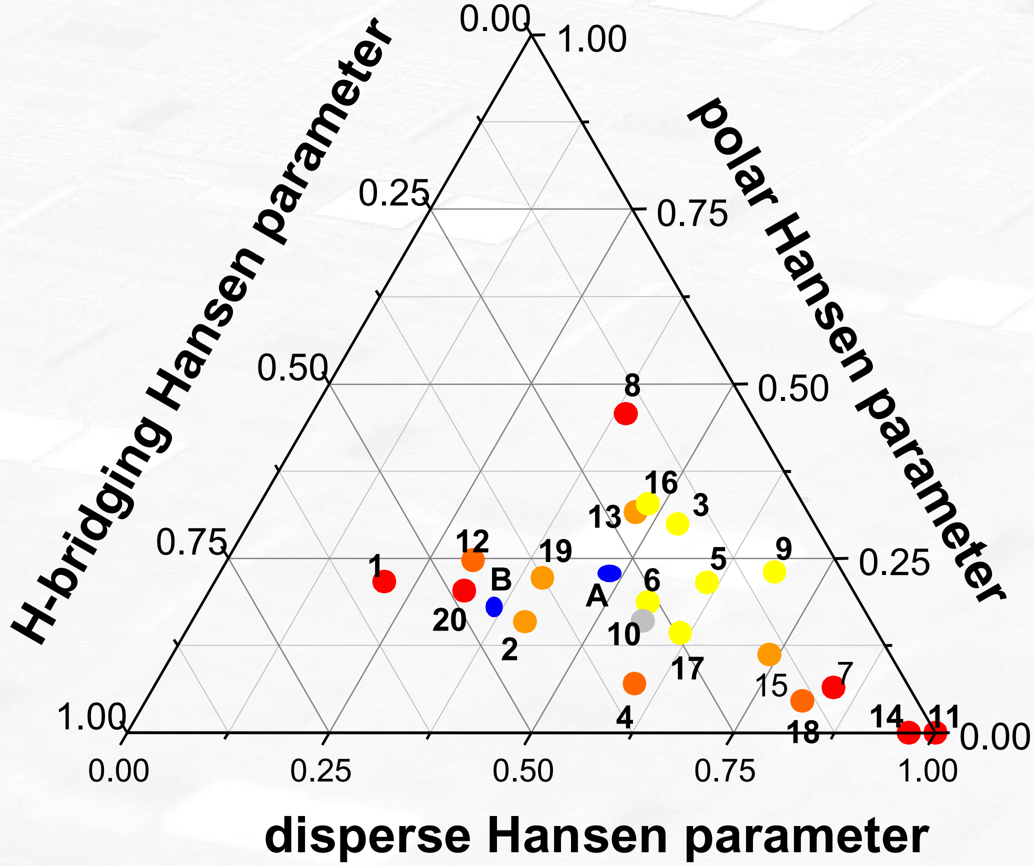
Solubility experimental results

The experiment indicates a region (yellow points) where the ratio of the Hansen's parameter have to be located to remove photoresist. Unfortunately crust and polymers are not addressed.



1	DI water
2	2-Propanol
3	2-Butanone
4	Dimethoxymethane
5	Cyclohexanone
6	Tetrahydrofurane
7	Toluene
8	Acetonitril
9	Chlorobutane
10	n-Propylamine
11	Hexane
12	Methanol
13	Acetone
14	Carbon Tetrachloride
15	Bromonaphthalene
16	N-methyl-2-pyrrolidone
17	n-Butylacetate
18	o-Xylene
19	Acetic acid
20	Ethylene glycol

no effect
minor effect
medium effect
total removal
not evaluable

A	Real Chem.1
B	Real Chem.2

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Characterization of the cleans chemistry
Dissolving parameter analysis theory

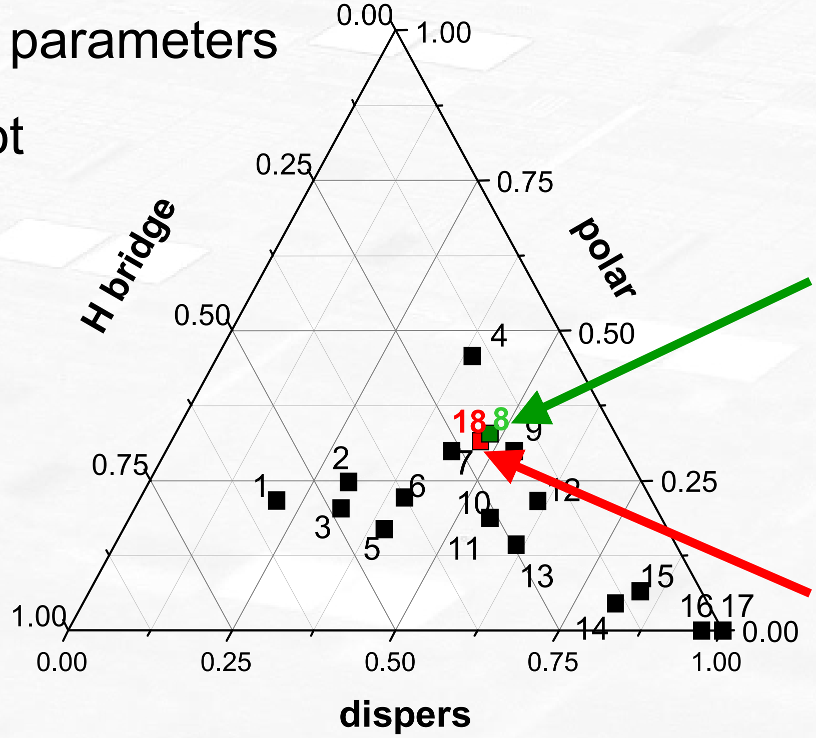
Hansen parameters	Basic properties of solution influencing the other parameters
Acidity	Availability of protons / hydroxide ions attacking solids and influencing parameters below
Fluoride activity	Attacks silicon-based materials
Redox potential	Attacks organic and metal-based material
Chelating properties	Improve solubility of metal ions

Characterization of the cleans chemistry
Dissolving Hansen parameter model

Example: ESH concerns about a problematic compound contained in some formulations, which worked well on a certain p-MSQ

Solubility parameters

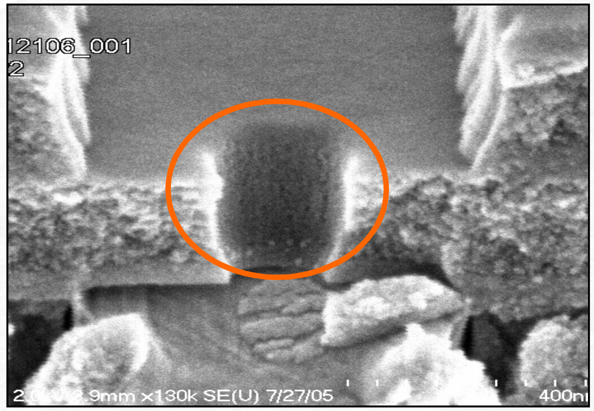
TEAS-plot



- 1 Water
- 2 Methanol
- 3 Ethylene glycol
- 4 Acetronitrile
- 5 1-Propanol
- 6 Acetic acid
- 7 Acetone
- 8 Alternative compound
- 9 Metyl-ethyl-ketone
- 10 Tetrahydrofuran
- 11 n-Propylamine
- 12 Cyclohexanone
- 13 n-Butyl acetate
- 14 o-Xylene
- 15 Toluene
- 16 Carbon tetrachloride
- 17 Hexane
- 18 Problematic compound

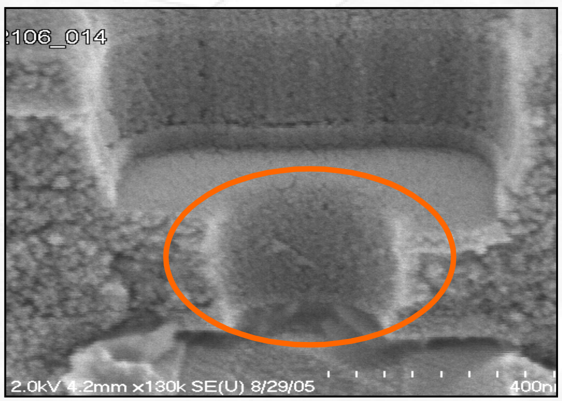
According to model, the alternative compound might be an alternative to the problematic compound, keeping all other compounds constant.

Characterization of the cleans chemistry
Dissolving Hansen parameter result

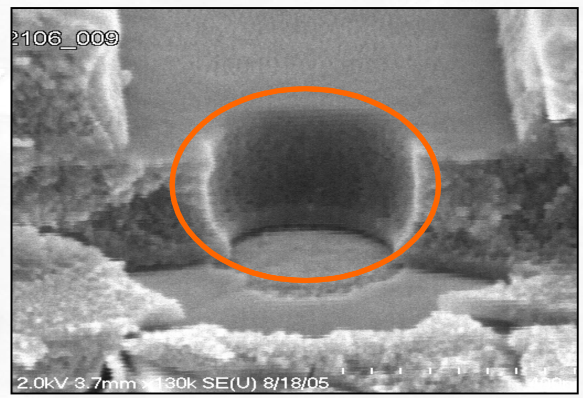


Before cleaning (wafer edge)

New version



Old version



Encouraging result!
New version containing alternative solvent could remove polymers from via bottom. Electrical test follows.

Characterization of the cleans chemistry
Dissolving data exchange tool I

Chemistry property calculator V2.1

Solvent

	Compound	CAS No	IONo	wt %
1	water	7732-18-5	869	25
2	Ethanol	64-17-5	768	25
3	glycerol	56-81-5	679	50
4		0	0	
5		0	0	
6		0	0	
7		0	0	
8		0	0	
9		0	0	
10		0	0	
11		0	0	
12		0	0	
13		0	0	
14		0	0	
15		0	0	

recommended Temperatur range

low	high
20	60

measured surface tension part

dispers	polar
13	25

measured viscosity

1.3

Chelating Potential		
Oxidizing Potential	[eV]	
Acidity	pH	
Fluoride concetration	[mol/l]	

The database contains at the moment 1000 compounds (solvents), which could be dialed by CAS No. or over 1500 names !!!!.

Supplier puts in formulation and measurement data

Characterization of the cleans chemistry
Dissolving data exchange tool II

Parameter List

TEAS parameters

fd	22.3
fp	24.6
fh	53.1

Cheletang Potential

	0

Oxidizing Potential

[eV]	0

Acidity

pH	0

Fluoride Concentration

[mol/l]	0

recommended Temperature range

low [C]	high [C]
20	60

measured surface tension

dispers [mN/m]	polar [mN/m]
13	25

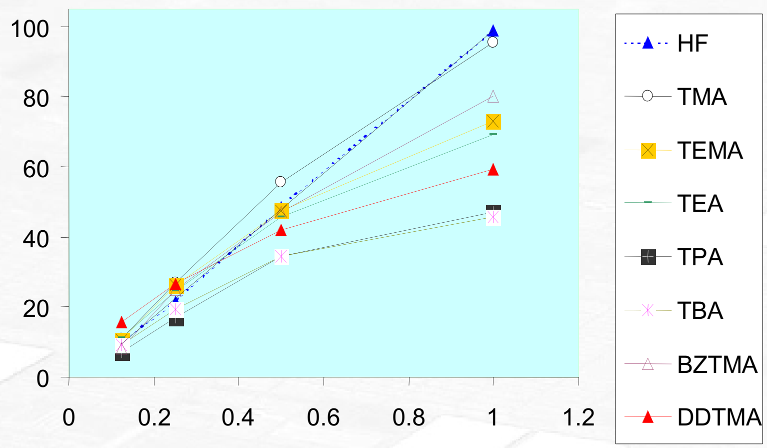
Viscosity

1.3

Only the calculated and measured data are delivered to the customer.

Fluoride activity – concentration effects

Etch Rate $(NR_4^+)(HF_2^-)$ (nominal) in H_20 versus Total [F] (Molality)-23 C @ 10 min



From Bill Wojtczak SACHEM INC.; SPCC, Austin, 2005.

Based on the original data provided by B. Wojtczak / Sachem Inc. a difference between diluted HF and bifluorides could be quantified:

1. **HF reacts in a first order; this means a linear correlation between F^- concentration and etch rate.**
2. **All bifluorides react in a second order; this means a linear correlation between nominal (F^- concentration)^2 and etch rate**
3. **Mathematical description for the correlations available**

Impact on semiconductor manufacturing:

Fluoride Buffer System

1. Bifluorides provide a suitable low level etch rate as a substitute for diluted HF.
2. Because of the lower slope in the correlation, the etch rate of solutions based on bifluorides should be less affected by fluoride consumption and therefore more stable.
3. Bifluorides offer a tuning capability due to the counter ion (ternary amine).

Characterization of the involved solids
Material parameters

With the introduction of carbon containing (mostly as Methyl-groups) materials, the history of a surface has much greater influence than before.

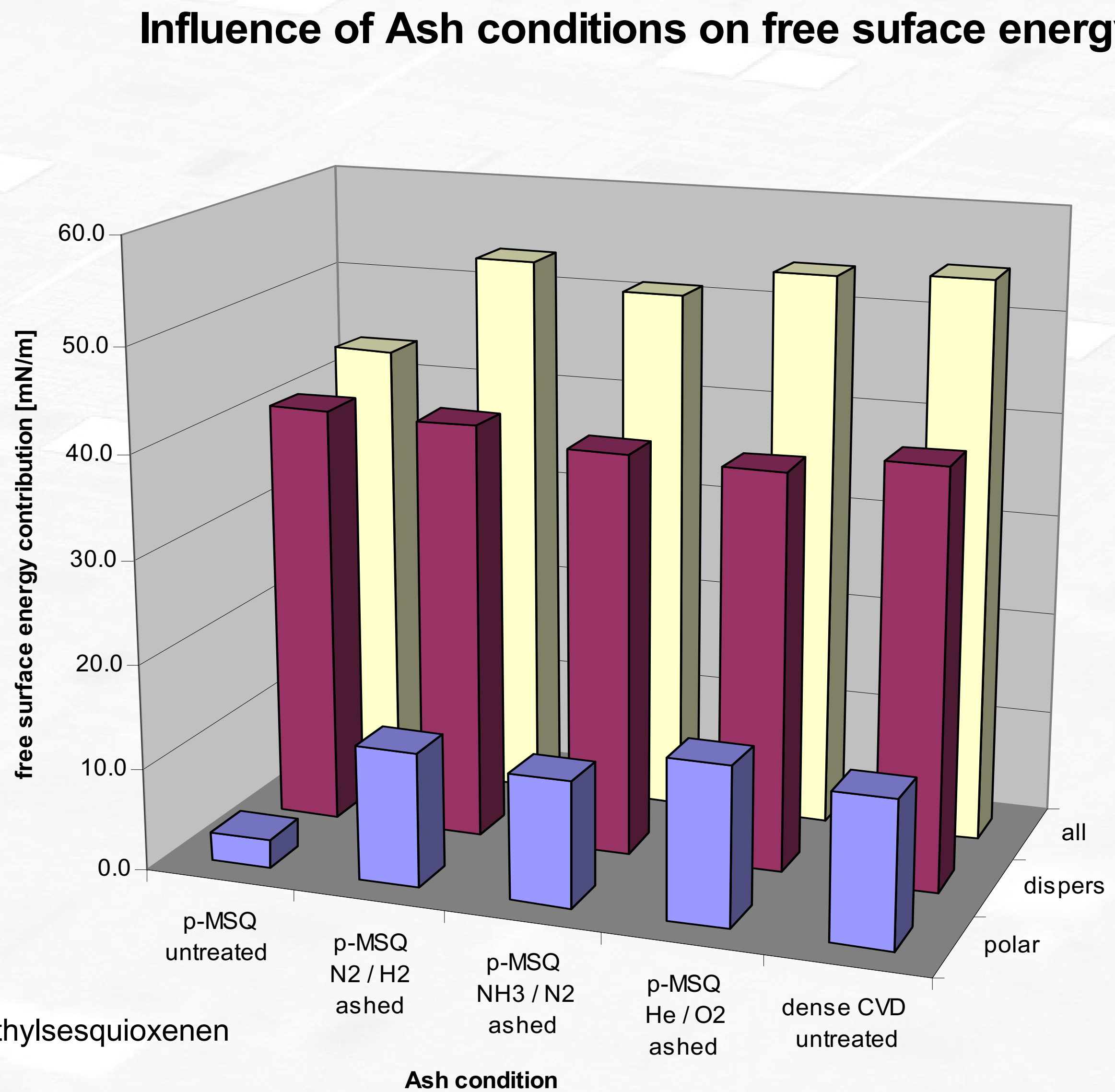
Wetting: Free surface energy

Each of the involved materials has to be characterized to determine the limit to which they can withstand the characteristic parameters of a liquid.

Parameters for dissolving/damage are as follows:

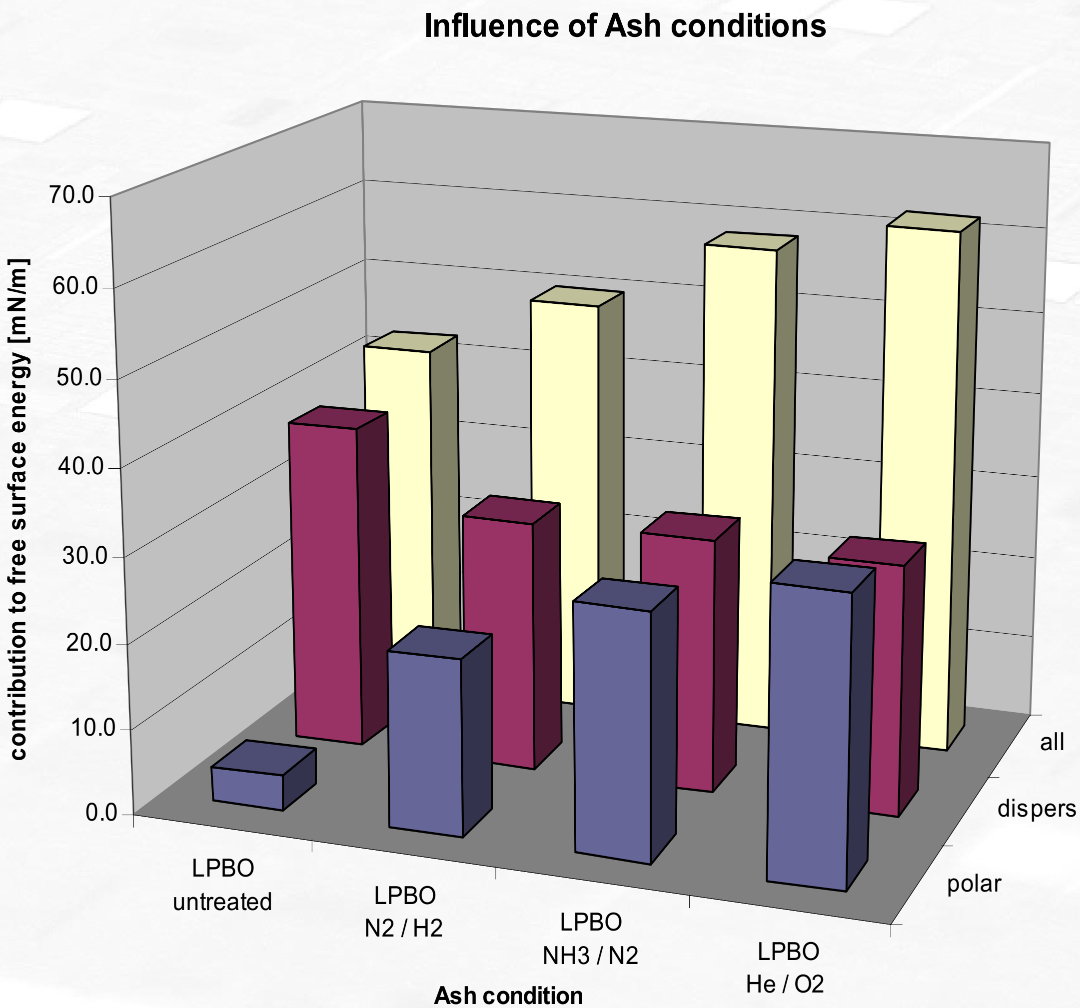
- Solubility parameters (Hansen)
- Acidity
- Fluoride activity
- Redox potential
- Chelating properties

Characterization of the involved solids
Wetting-polar and disperse part of surface tension



p-MSQ: porous Methylsesquioxenen

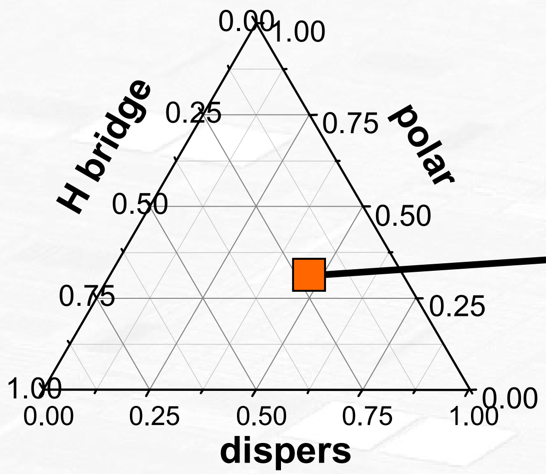
Characterization of the involved solids
Wetting-polar and disperse part of surface tension

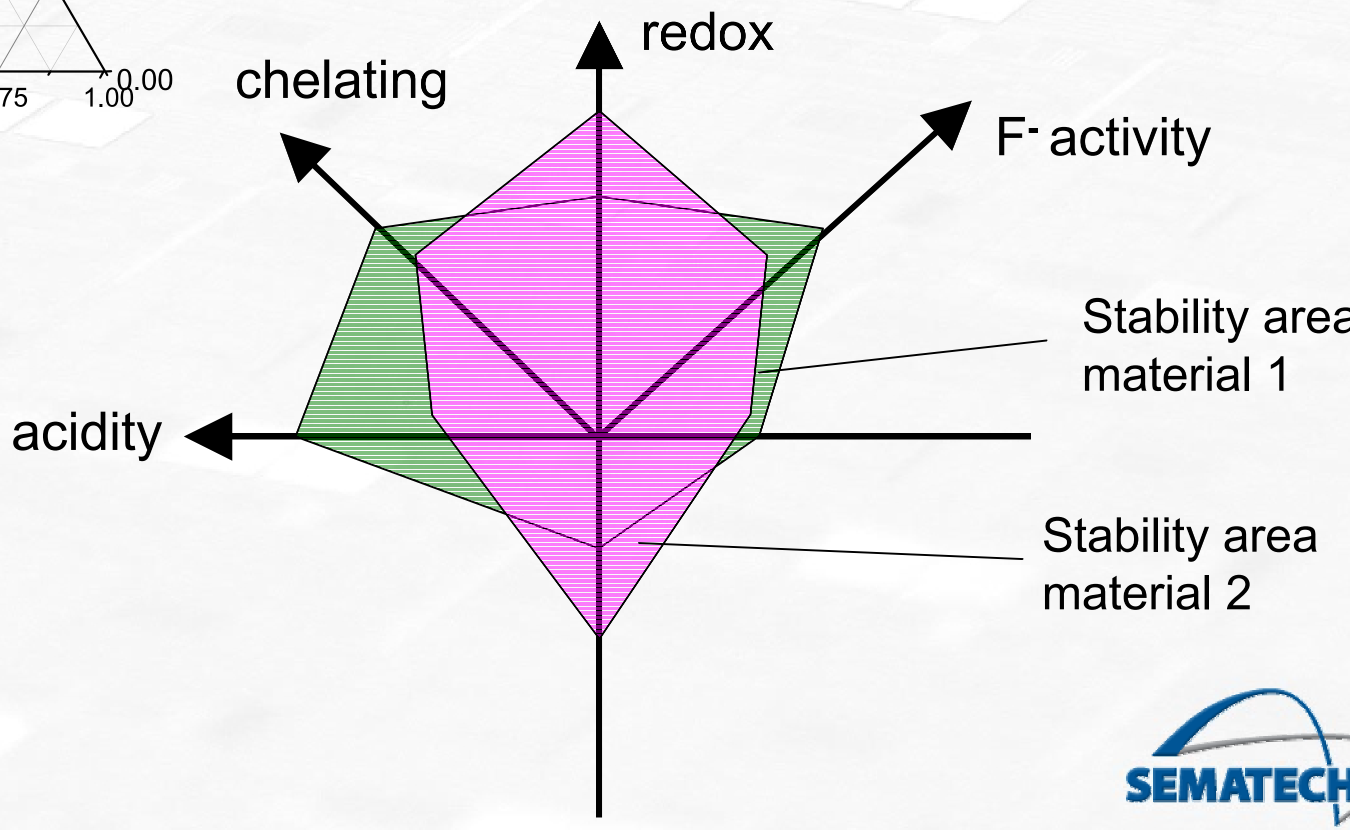


LPBO: late porogen burn out

Characterization of the involved solids

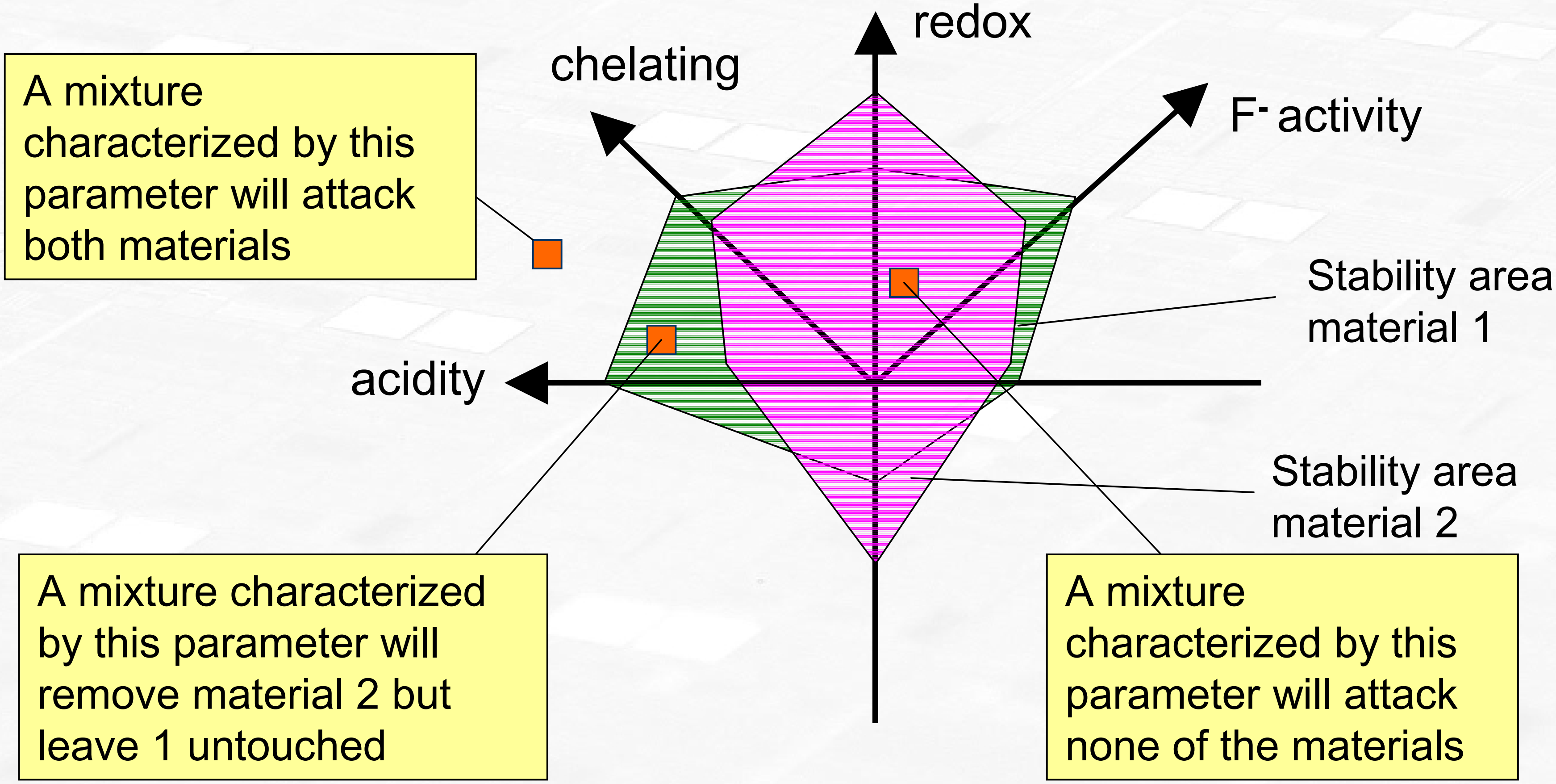
Solvent system (plain or mixture)





Characterization of the involved solids

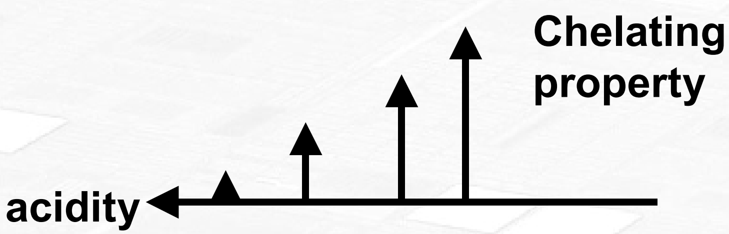
How to use (neglecting interactions)



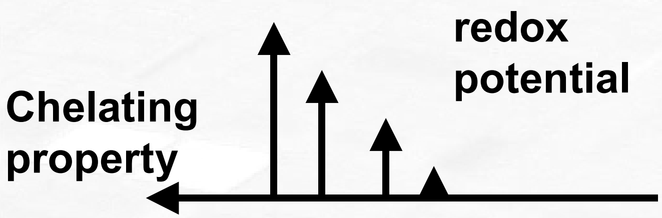
Characterization of the involved solids
Regarding interactions overall rules

The solvent is influencing and is influenced by the other parameters.

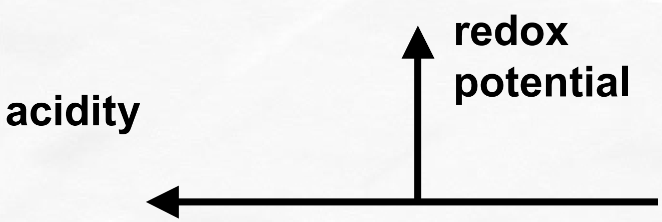
e.g., Protonation of amine groups, deprotonation of carbonic acid groups



Because protons compete with metal ions, the chelating property normally drops at higher acidity.



The better reaction products like metal ions get dissolved, the lower the redox stability.



Depending on the system, acidity has a large effect on the redox potential.

Summary I

For

- faster
- resource saving
- cheaper
- IP safer

For development, it is necessary to have an

- formulation independent
- standardized

way to describe cleans chemistries.

Summary II

A parameter set to describe chemical formulations has been developed. These consist of

- Solubility parameters (Hansen)
- Acidity
- Fluoride activity
- Redox potential
- Chelating properties

The concept of material stability areas was introduced.

A calculator has been developed to calculate the Hansen's parameter of the solvent part of mixtures. An encouraging result has been achieved.

Future work

The interactions among the parameters have to be investigated, especially

- Acidity-Redox-Solvent
- Acidity-Solvent-Fluoride Activity
- Acidity-Chelating-Solvent

The stability areas of all materials used in semiconductor manufacturing must be acquired.

The measurement techniques for the parameters must be standardized.